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Bonded atoms in sodium chloride – the information-theoretic approach

Roman F. Nalewajski, Rafał Loska

Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland

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Abstract. The information-theoretic approach to the classical problem of partitioning the molecular electron density, ρ, into densities $\{\rho_\alpha\}$ of the bonded atoms in molecules (AIM) is briefly summarized. The minimization of the missing information (entropy deficiency) between the isolated atom densities, $\{\rho_\alpha^0\}$, which define the promolecule density, ρ^0, of the molecular density difference diagrams, $\Delta\rho = \rho - \rho^0$, and the AIM densities $\{\rho_\alpha\}$ in an exhaustive partitioning of ρ gives rise to the "stockholder" scheme of Hirshfeld. A related nonexhaustive approach is also outlined and the polarized (closed) atom densities in a molecule are obtained by simultaneously minimizing their information distance with respect to both the isolated and the Hirshfeld atomic densities. For neutral molecules these schemes are unique when the ground-state densities of isolated atoms are selected as a reference. In an attempt to validate this natural choice two sets of the stockholder atoms in NaCl, resulting from the ground-state ionic ($Na^+ + Cl^-$) and atomic ($Na + Cl$) promolecule references, respectively, are compared and found to be almost identical. Small differences observed in the asymptotic, low-density regions are interpreted in terms of the reverse direction of the molecular charge transfer with respect to these initial promolecule states. A concept of the molecularly promoted reference corresponding to the promolecule density involving the statistical mixture of ionic and atomic densities, with the ensemble probabilities minimizing the deviations between the ensemble and molecular densities, is introduced.

Key words: Atomic densities – Atoms in molecules – Charge transfer – Chemical bond – Entropy deficiency

1 Introduction

In chemical interpretations of the electronic structure of molecular systems the concepts of atoms in molecules (AIM) and that of the bonds connecting AIM are of paramount importance [1–22]. The AIM electron densities, obtained either by an appropriate partitioning of the physical space [6, 7] or by the function space division of the molecular density [2, 8, 9], determine the effective AIM charges (oxidation states), while the bond-multiplicity indices [5, 10–22] provide a generalized structural formula of the system under consideration. A great deal of effort has been devoted in quantum chemistry to devise adequate measures of these elusive concepts, originally introduced on basically intuitive grounds, in such a way that they reproduce the established chemical intuition in standard molecules and processes [2–22].

It has been demonstrated recently [23, 24] that both these concepts can be successfully tackled within information theory [25–28]. The AIM information entropic development, which we briefly summarize in Sect. 2, is based on the premise of the exhaustive partitioning of molecular density and the requirement that the AIM densities, being only slightly perturbed in their valence shell relative to the corresponding isolated atoms, should minimize the information distance (missing information, entropy deficiency) of Kullback and Leibler [26] relative to the reference densities of separated, nonbonded atoms of the periodic table. Let us recall that these isolated atom densities also define the so-called promolecule density of the analysis of changes in the electron distribution due to the chemical bond formation in terms of the familiar density difference diagrams. Such an approach generates the Hirshfeld [9] partitioning scheme of the known molecular density, determined theoretically or experimentally, into the so-called "stockholder" atoms. The latter thus appear as unbiased pieces of density, which are the least distant in their information content from their isolated atom analogs.

The Hirshfeld partitioning is unique, provided there is no ambiguity in the choice of the promolecule density, i.e., of the corresponding separated atom/ion limit

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Correspondnece to: R. F. Nalewajski

(SAL). The obvious SAL selection for a neutral molecular system is the set of the ground-state densities of isolated atoms. This is indeed a natural choice when the dissociation of a molecule into constituent atoms proceeds along a single potential-energy surface. In some instances, however, for example in alkali halides, such bond-breaking process involves both atomic and ionic electronic states. For such a case the question arises, how different are the stockholder atoms corresponding to these two SAL choices?

It is the main purpose of the present study to investigate the degree of dependence of the stockholder bonded atoms on the choice of the ionic or atomic promolecule reference densities in the illustrative case of NaCl. It should be stressed, that these two references must reflect different directions of the charge transfer (CT), ionic (CT_i) $Na^+ \leftarrow Cl^-$ and atomic (CT_a) $Na \rightarrow Cl$, respectively, which are required to generate the final, molecular distribution of the electronic charge from the selected initial, promolecular states. We search for possible manifestations of these reverse CT directions in the resulting densities of the Hirshfeld atoms.

In Sect. 2 we also use information theory to define the atomic densities at the intermediate, polarization stage of the bond-formation process in a molecule. We accomplish this within a nonexhaustive division scheme by minimizing the information distance between the densities of the closed (polarized only) atoms in a molecule with respect to the densities of both the isolated atoms and the open, Hirshfeld AIM, subject to the separate atomic closure conditions. Finally, we address a more general problem of establishing the unique, molecularly promoted promolecule reference for alkali halides, by defining an appropriate statistical mixture (SAL ensemble) of the ionic and atomic promolecule densities. Atomic units are used throughout.

2 Summary of the information-theoretic development

2.1 Exhaustive, Hirshfeld partitioning scheme

Consider a molecular system $\mathscr{M}(\mathbf{R})$ consisting of m atoms, with the nuclei at the fixed positions $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_m) \equiv \{\mathbf{R}_\alpha\}$. The so-called "stockholder" partitioning of Hirshfeld divides the molecular electron density, $\rho(\mathbf{r})$, into the densities $\{\rho_\alpha(\mathbf{r})\}$ of AIM,

$$\begin{aligned}\rho_\alpha(\mathrm{r};\mathbf{R}_\alpha) &= \rho(\mathbf{r})[\rho^0_\alpha(\mathbf{r}-\mathbf{R}_\alpha)/\rho^0(\mathbf{r})] \equiv \rho(\mathbf{r})\omega_\alpha(\mathbf{r}) \\ &\equiv \rho^0_\alpha(\mathbf{r}-\mathbf{R}_\alpha)D(\mathbf{r}) \equiv \rho_\alpha(\mathbf{r}), \quad \alpha = 1,2,\ldots,m,\end{aligned} \tag{1}$$

in accordance with the local atomic share factor $\omega_\alpha(\mathbf{r})$ given by the ratio of the isolated atom density $\rho^0_\alpha(\mathbf{r} - \mathbf{R}_\alpha)$ and the reference density

$$\rho^0(\mathbf{r};\mathbf{R}) = \sum_{\alpha=1}^{m} \rho^0_\alpha(\mathbf{r}-\mathbf{R}_\alpha) \equiv \rho^0(\mathbf{r}) \ , \tag{2}$$

of the promolecule $\mathscr{M}^0(\mathbf{R})$, consisting of the densities $\{\rho^0_\alpha(\mathbf{r})\}$ in the atomic SAL (SAL-a) shifted to the nuclear positions $\mathbf{R}$ in the molecule. The same atomic promolecule density provides a reference for generating the familiar density difference diagrams, $\Delta\rho(\mathbf{r};\ \mathbf{R}) = \rho(\mathbf{r}) - \rho^0(\mathbf{r})$, reflecting changes in the electron density due to the formation of the chemical bonds in a molecule.

It has been demonstrated recently [23] that this AIM discretization scheme has a sound basis in information theory. More specifically, the Hirshfeld atomic densities $\{\rho_\alpha\}$ minimize the entropy deficiency (missing information) of Kullback and Leibler [26] with respect to the isolated atom densities of the promolecule,

$$\Delta S(\{\rho_\alpha\}|\{\rho^0_\alpha\}) = \sum_{\alpha=1}^{m} \int \rho_\alpha(\mathbf{r}) \ln[\rho_\alpha(\mathbf{r})/\rho^0_\alpha(\mathbf{r}-\mathbf{R}_\alpha)]\mathrm{d}\mathbf{r} \ , \tag{3}$$

subject to the local constraint of the exhaustive division of the molecular density

$$\sum_{\alpha=1}^{m} \rho_\alpha(\mathbf{r}) = \rho(\mathbf{r}) \ . \tag{4}$$

This can be easily verified by multiplying the local constraint of Eq. (4) by the local Lagrange multiplier, $\lambda(\mathbf{r})$, and by adding the product to the information entropy functional of Eq. (3) to obtain the auxiliary functional, in which the AIM densities are fully independent. The resulting Euler equation for the best atomic densities of this constrained variational principle,

$$\begin{aligned}&\sum_{\alpha=1}^{m} \{\ln[\rho_\alpha(\mathbf{r})/\rho^0_\alpha(\mathbf{r}-\mathbf{R}_\alpha)] - [\lambda(\mathbf{r})-1]\}\delta\rho_\alpha(\mathbf{r}) \\ &\quad \equiv \sum_{\alpha=1}^{m} \ln\{\rho_\alpha(\mathbf{r})/[\rho^0_\alpha(\mathbf{r}-\mathbf{R}_\alpha)d(\mathbf{r})]\}\delta\rho_\alpha(\mathbf{r}) = 0,\end{aligned} \tag{5}$$

where $\ln d(\mathbf{r}) \equiv \lambda(\mathbf{r}) - 1$, gives

$$\begin{aligned}&\ln \rho_\alpha(\mathbf{r})/[\rho^0_\alpha(\mathbf{r}-\mathbf{R}_\alpha)d(\mathbf{r})] = 0, \quad \text{or} \\ &\rho_\alpha(\mathbf{r}) = \rho^0_\alpha(\mathbf{r}-\mathbf{R}_\alpha)d(\mathbf{r}) \equiv \rho_\alpha(\{\rho^0_\alpha\},\ \rho).\end{aligned} \tag{6}$$

The local proportionality factor $d(\mathbf{r})$, determined from Eq. (4), is indeed the same as in Eq. (1):

$$d(\mathbf{r}) = \rho(\mathbf{r})/\rho^0(\mathbf{r}) = D(\mathbf{r}) \ . \tag{7}$$

Therefore, the "stockholder" bonded atoms of Hirshfeld minimize the information distance between the electron distributions of AIM and those of the isolated atoms in the SAL-a, which define the promolecule reference. These atomic building blocks preserve as much information as possible about the separated atoms, thus being firmly tied to the periodic table of elements. These atomic densities are known to yield fairly transferable charge distributions and moments, which can be used in calculations of the molecular electrostatic potential and the interaction energy. The division scheme is basis-set independent and it applies to both theoretical and experimental densities. The resulting AIM densities exhibit a single cusp at the atom nucleus, decaying exponentially with increasing distance from it. They also equalize their chemical potentials at the global, molecular chemical potential (negative electronegativity) level, as required by the Sanderson [29] principle and the density functional theory variation principle [8, 30–32].

2.2 Nonexhaustive division scheme

Yet another set of AIM densities $\{\bar\rho_\alpha\}$ results from the modified minimum entropy deficiency principle, in which only the overall number of electrons in $\mathscr{M}$,

$$N=\sum_{\alpha=1}^{m}\int\bar\rho_\alpha(\mathbf{r})\mathrm{d}\mathbf{r}=\sum_{\alpha=1}^{m}\int\rho_\alpha^0(\mathbf{r})\mathrm{d}\mathbf{r}\equiv\sum_{\alpha=1}^{m}N_\alpha^0\equiv N^0\ ,\qquad(8)$$

is fixed, instead of constraining the sum of AIM densities, $\sum_{\alpha=1}^{m}\bar\rho_\alpha(\mathbf{r})=\bar\rho(\mathbf{r})$, to exactly reproduce $\rho(\mathbf{r})$. In such an approach one uses the molecular and promolecule densities as the two fixed references and searches for the densities of AIM which simultaneously give the maximum likeness, in the information-theoretic sense, to both of them. Clearly, the sum of such bonded, open-atom solutions of the associated variational procedure will not be identical with any of the two reference densities; instead it will represent some "transition" density between ρ and ρ^0. More specifically, one may insist on $\bar\rho$ to be also the least distant in information entropy terms from ρ by adding to the entropy deficiency of Eq. (3) the extra missing information term measuring this very information distance:

$$\begin{aligned}&\Delta\bar S(\{\bar\rho_\alpha\}|\{\rho_\alpha^0\},\ \rho)\\&\quad=\Delta S(\{\bar\rho_\alpha\}|\{\rho_\alpha^0\})+\int\bar\rho(\mathbf{r})\ln[\bar\rho(\mathbf{r})/\rho(\mathbf{r})]\mathrm{d}\mathbf{r}\ .\end{aligned}\qquad(9)$$

As shown elsewhere [23], the variational principle,

$$\delta\left[\Delta\bar S(\{\bar\rho_\alpha\}|\{\rho_\alpha^0\},\ \rho)-\lambda\int\bar\rho(\mathbf{r})\mathrm{d}\mathbf{r}\right]=0\ ,\qquad(10)$$

gives the optimum densities $\{\bar\rho_\alpha\}$ which are "halfway" promoted from the corresponding isolated atom densities towards the fully molecular AIM densities, $\{\rho_\alpha\}$, of the Hirshfeld AIM:

$$\begin{aligned}&\bar\rho_\alpha(\mathbf{r})=C\rho_\alpha^0(\mathbf{r}-\mathbf{R}_\alpha)[D(\mathbf{r})]^{1/2}\equiv\bar\rho_\alpha(\{\rho_\alpha^0\},\ \rho),\\&\qquad C=N^0/\int[\rho(\mathbf{r})\rho^0(\mathbf{r})]^{1/2}\mathrm{d}\mathbf{r}\cong1\ .\end{aligned}\qquad(11)$$

The corresponding overall molecular density is then proportional to the geometric average of the promolecule and molecular density:

$$\bar\rho(\mathbf{r})=C\left[\rho(\mathbf{r})\rho^0(\mathbf{r})\right]^{1/2}\equiv C\rho^{\mathrm{g}}(\mathbf{r})\ .\qquad(12)$$

In this article we also investigate how close this average is to the molecular density when the atomic and ionic promolecule densities of NaCl are used in such a nonexhaustive partitioning scheme.

2.3 Molecularly promoted, polarized atoms

In physical interpretations of origins of the chemical bond an intermediate, polarization stage of the bond formation is often considered, when atoms are free to adjust their charge distributions to a changed, molecular environment without the freedom to exchange electrons (zero CT). In other words, the densities $\{\tilde\rho_\alpha\}$ of such polarized, closed atoms should retain as much as possible of the information contained in both the initial atomic densities, $\{\rho_\alpha^0\}$, and in the final atomic densities, $[\rho_\alpha(\{\rho_\alpha^0\},\ \rho)]$ (Eq. 6) of the open Hirshfeld atoms.

The polarized atoms correspond to the regional (intraatomic), polarization equilibrium in a molecule, while the Hirshfeld atoms, which equalize atomic electronegativities (negative chemical potentials) [23], represent the global (interatomic), CT equilibrium of the molecular system under consideration [32].

The optimum densities of such polarized (molecularly promoted), closed atoms follow from the minimization of the entropy deficiency function,

$$\begin{aligned}&\Delta\tilde S[\{\tilde\rho_\alpha\}|\{\rho_\alpha^0\},\{\rho_\alpha(\{\rho_\alpha^0\},\ \rho)\}]\\&\quad=\Delta S(\{\tilde\rho_\alpha\}|\{\rho_\alpha^0\})+\Delta S[\{\tilde\rho_\alpha\}|\{\rho_\alpha(\{\rho_\alpha^0\},\ \rho)\}]\ ,\end{aligned}\qquad(13)$$

subject to the separate atomic closure constraints

$$\int\tilde\rho_\alpha(\mathbf{r})\mathrm{d}\mathbf{r}=N_\alpha^0,\quad\alpha=1,2,\ldots m\ .\qquad(14)$$

The Euler–Lagrange variational principle,

$$\delta\left\{\Delta\tilde S[\{\tilde\rho_\alpha\}|\{\rho_\alpha^0\},\{\rho_\alpha(\{\rho_\alpha^0\},\rho)\}]-\sum_{\alpha=1}^{m}\lambda_\alpha\int\tilde\rho_\alpha(\mathbf{r})\mathrm{d}\mathbf{r}\right\}=0,\qquad(15)$$

then gives the renormalized geometric average of the isolated and Hirshfeld atom densities:

$$\begin{aligned}&\tilde\rho_\alpha(\{\rho_\alpha^0\},\ \rho)=C_\alpha\left(\rho_\alpha^0\rho_\alpha\right)^{1/2}\equiv\tilde\rho_\alpha(\{\rho_\alpha^0\},\ \rho),\\&\qquad C_\alpha=\left[N_\alpha^0/\int\left(\rho_\alpha^0\rho_\alpha\right)^{1/2}\mathrm{d}\mathbf{r}\right]\cong1\ .\end{aligned}\qquad(16)$$

This result is similar to that of Eq. (12). When the entropy function calls for the maximum similarity, i.e., the minimum missing information (minimum entropy deficiency), of the optimized function to the two known functions it predicts as the optimum solution the geometric average of these two references. In a sense this is a "transition" function, "halfway" between the two fixed reference functions. This geometric mean rule was also observed earlier in an isomorphic problem of molecular similarity [23].

With these examples we believe we have demonstrated the versatility of the information-theoretic partitioning of the molecular electronic density and its use in defining both the intermediate and final stages of the atomic charge reconstruction in a molecule.

2.4 Atomic versus ionic dissociation limits

The Hirshfeld and related partitioning schemes are unique provided there is no ambiguity concerning the choice of the promolecule. In some cases, however, for example in the alkali-metal halides MX, for example $M=\mathrm{Na}$ and $X=\mathrm{Cl}$, this is not the case, since both ionic and atomic SAL can be invoked. In the $M\overset{R}{-}X$ case the molecular ground-state is the ionic potential-energy curve $E_{\mathrm{i}}(R)$, yielding the excited, ionic dissociation limit $M^+ + X^-$ (SAL-i) for large internuclear distance $R\to\infty$, while the lowest, atomic dissociation limit,

$M + X$ (SAL-a), is the molecular excited, atomic potential-energy curve, $E_a(R)$, with the energy gap between the two SAL states determining the global electronic hardness η^0_{M+X} for the SAL-a system $\mathscr{M}(\infty)$ of the two isolated atoms:

$$E_i(\infty) - E_a(\infty) = I^0_M - A^0_X = \eta^0_{M+X}; \qquad (17)$$

Here I^0_M, A^0_X stand for the ionization potential and the electron affinity of the isolated M and X atoms, respectively.

In such a case the question naturally arises: which of the two promolecule choices, the atomic, ρ^0_a, using the densities of the SAL-a, or the ionic, ρ^0_i, using the densities of the ionic pair in the SAL-i, is more appropriate to characterize bonded atoms? One would also be interested in examining the differences in the corresponding AIM densities and their effect on the description of the SAL density reorganization in a molecule due to the intraatomic polarization and the interatomic CT.

This question is also related to the problem of the general applicability of the atomic references used in the typical Hirshfeld procedure. Namely, should the observed differences be found negligible, at least within a molecule, one could then indeed fix the reference promolecule density as consisting of atomic densities in all cases. This natural assumption would also unify the definition of the CT by linking it to the initial atomic states only.

Here we examine in some detail how strongly the Hirshfeld atoms depend on the choice of the promolecule reference density, selecting NaCl as an illustrative example. We also compare the differences between the molecular and the two promolecule densities, i.e., the corresponding density difference functions $\Delta\rho_a$ and $\Delta\rho_i$. Also of interest to us are deviations of the geometric mean densities, $(\rho\rho^0_s)^{1/2}$, (Eq. 12) from the molecular density, ρ, for the two SAL choices $s = \text{a,i}$.

3 Illustrative analysis for sodium chloride

3.1 Calculations and results

The standard local spin density approximation calculations of the Kohn–Sham (KS) [33] density functional theory were carried out, using the deMon program [34] and the double-zeta valence basis set, to generate the ground-state molecular and atomic/ionic electron densities, for the KS-optimized bond length, $R^{KS}_e = 4.49$, close to the experimental equilibrium value, $R_e = 4.46$. The calculated density profiles corresponding to the bond-axis cut of the molecular and atomic densities in NaCl are compared in Figs. 1, 2, 3, and 4.

Logarithmic plots of the two promolecule densities ρ^0_a and ρ^0_i are compared with the molecular density ρ in Fig. 1A, while the actual displacements of these promolecule densities from ρ are displayed along the bond axis in Fig. 1b, in order to see which promolecule reference density is "closer" to the final, molecular density and how this identification changes with the distance from the bonding region. The geometric averages of Eq. (12), $\rho^g_s = (\rho\rho^0_s)^{1/2}$, s = a,i, are compared against ρ in Fig. 2: the density differences in the bonding region are shown in Fig. 2A; these differences are displayed for a wider range of electron positions along the bond axis in Fig. 2B. Next two figures report plots of the resulting densities of the Hirshfeld atoms for the two SAL choices, $[\rho_\alpha(\rho^0_s), s = \text{a,i}]$; α = Na (Fig. 3) and Cl (Fig. 4). They are compared with the corresponding isolated atom or ion reference densities in panels A and B, respectively, and the AIM densities from the two promolecules are compared in panel C of each figure.

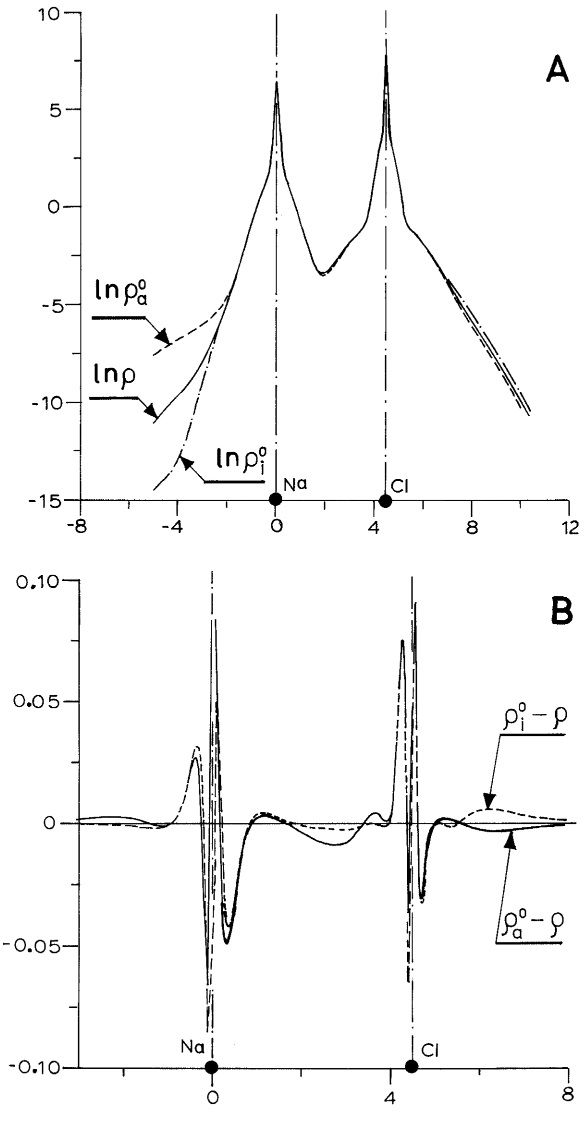


Fig. 1A, B. A comparison of the molecular density $\rho(\mathbf{r})$ of NaCl with the atomic, $\rho^0_a(\mathbf{r})$, and ionic, $\rho^0_i(\mathbf{r})$, promolecule densities, corresponding to the dissociation limits Na + Cl (SAL-a) and Na^+ + Cl^- (SAL-i), respectively. **A** Logaritmic plots of the density profiles for the cut along the bond axis. **B** The corresponding deviations of the two promolecule density profiles from that of the molecular density (negative density difference plots $\Delta\rho_a$ and $\Delta\rho_i$). The density profiles in all the other figures correspond to the the same cut including the Na–Cl axis

4 Discussion

4.1 Promolecule densities

It follows from the negative density difference diagrams of Fig. 1B that in the bonding region the ionic promolecule density is much closer to the molecular density than the corresponding atomic promolecule. Near the nuclei they both exhibit large oscillations from the molecular reference density, reflecting the shell structure of each atom. Obviously, this is a manifestation of the orbital relaxation due to the $\mathrm{Na}^0 \xrightarrow{\mathrm{CT_a}} \mathrm{Cl}^0$ effective atomic CT in a molecule, relative to the atomic dissociation limit: Na + Cl.

It should be emphasized, however, that since the fractional charge δ of the sodium atom in NaCl is in fact close to unity, $0 < \delta \lesssim 1$, the ionic promolecule reference $\mathrm{Na}^{+1} + \mathrm{Cl}^{-1}$ predicts the reverse, and much smaller $\mathrm{Na}^{+1} \xleftarrow{\mathrm{CT_i}} \mathrm{Cl}^{-1}$ ionic CT, correcting for a slightly too large charge separation in this ionic dissociation limit.

One finds manifestations of these reverse directions of both CTs in the nonbonding parts of both panels of Fig. 1. For example, a reference to Fig. 1B shows that the molecular density in the nonbonding region of the sodium atom is below (above) the atomic (ionic) promolecule density. In other words, there is an excess electron density, relative to the corresponding molecular value, on the nonbonding side of the neutral sodium atom, and the opposite is observed in the sodium cation case. The opposite trend is observed accordingly on the nonbonding side of the chlorine atom.

The same conclusion follows from the logarithmic plots, which emphasize the regions of very small density values, and especially the asymptotic decay regions of the two atoms. It also extracts the shell structure of each atom, reflecting the approximately piecewise exponential character of the atomic densities in each shell.

Figure 1 demonstrates that the atomic and ionic promolecule densities provide excellent reference densities for the Hirshfeld partitioning, both being very close to the molecular density in practically the whole molecular region of appreciable density values. They both deviate from the molecular density mainly in the asymptotic regions, of very low density values. In the vicinity of nuclei, where the density reaches very high values, the oscillations shown in panel B constitute a very small fraction of the density absolute value, as is indeed seen in Fig. 1A. These observations indicate that both these promolecules should generate almost identical Hirshfeld AIM for the same molecular density.

4.2 Geometric averages of the molecular and promolecule densities

As we have demonstrated in Sect. 2 the nonexhaustive partitioning scheme gives rise to the density $\bar{\rho}_s \cong \rho_s^{\mathrm{g}} =$

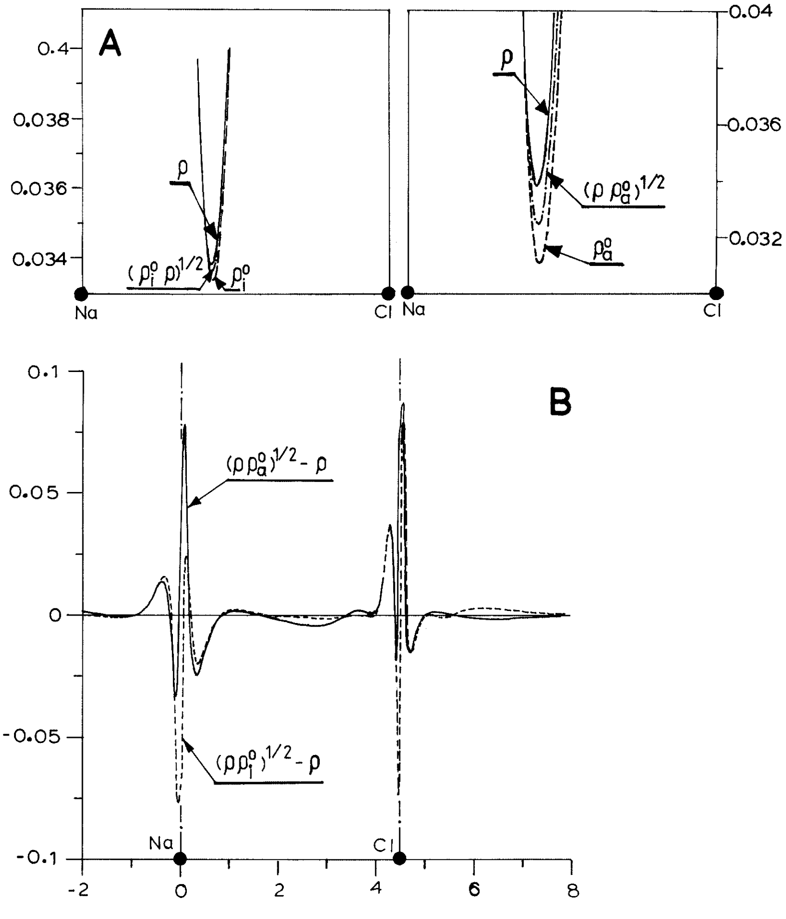
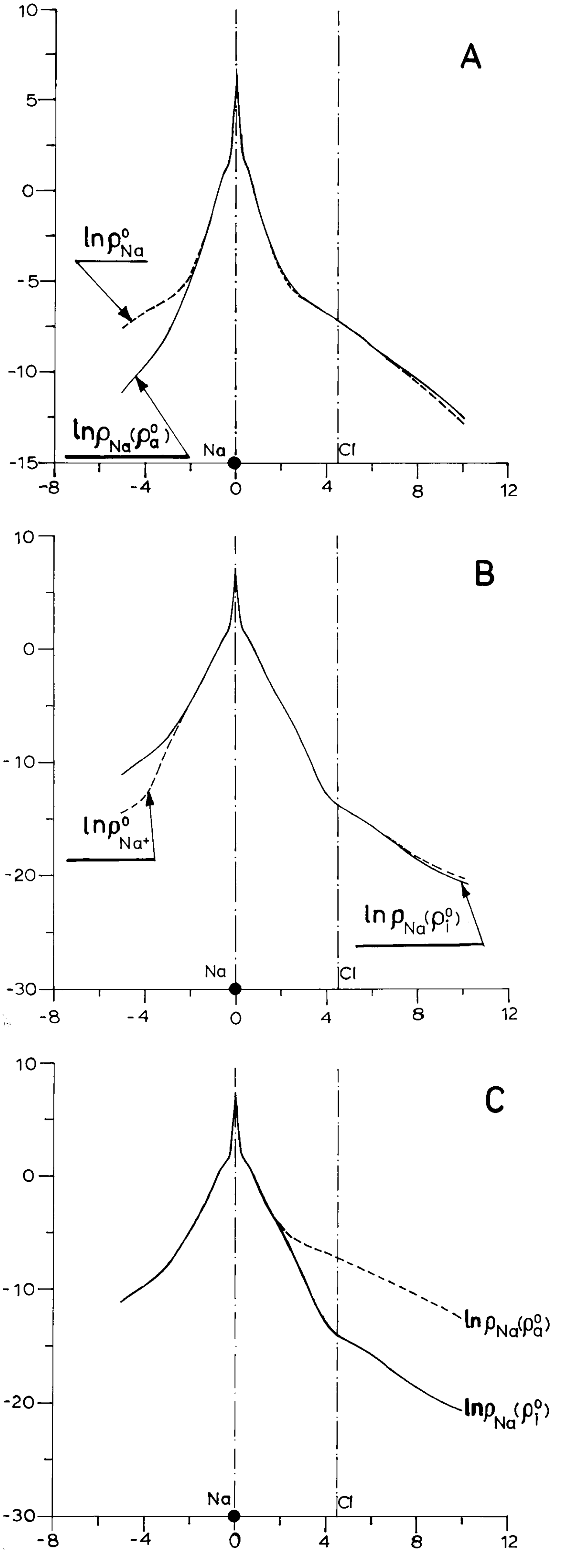


Fig. 2A, B. A comparison of the geometric averages of the molecular and promolecule densities: $(\rho\rho_s^0)^{1/2}$, $s =$ a,i. **A** The density profiles in the bonding region. **B** The deviations of the average densities from the molecular density



◄

Fig. 3A–C. The logarithm of the density profile of the Hirshfeld ("stockholder") sodium atom in NaCl for the atomic and ionic promolecule densities. **A** The atomic density from the atomic promolecule, $\rho_{\mathrm{Na}}(\rho_a^0)$, compared with the isolated atom density, ρ^0_{Na}, of SAL-a. **B** The AIM density from the ionic promolecule reference, $\rho_{\mathrm{Na}}(\rho_{\mathrm{i}}^0)$, compared with the isolated Na$^+$ density, $\rho^0_{\mathrm{Na}^+}$, of SAL-i. **C** The Hirshfeld AIM densities from the two promolecule references

$(\rho\rho_s^0)^{1/2}$, $s = $ a,i, which is already "halfway" modified from the initial, promolecule density towards the final, molecular density. The geometric means, $\{\rho_s^{\mathrm{g}}\}$, are compared with the molecular density, ρ, in Fig. 2. Since the ionic promolecule density, ρ_{i}^0, has been found to be generally a bit closer to ρ than the atomic promolecule density, ρ_{a}^0, one should also expect the $\rho_{\mathrm{i}}^{\mathrm{g}}$ to be, on average, less distant from ρ than $\rho_{\mathrm{a}}^{\mathrm{g}}$. This prediction is indeed supported by both panels of Fig. 2. In particular, both diagrams indicate that in the crucial bonding region the $\rho_{\mathrm{i}}^{\mathrm{g}}$ function provides a much better representation of the molecular density. In Fig. 2B we again discover a manifestation of the reverse CTs relative to the atomic and ionic dissociation limits, respectively, although this is emphasized less in comparison to Fig. 1B; also relatively reduced are the amplitudes of the inner-shell oscillations of the differences between the geometric mean and the molecular densities.

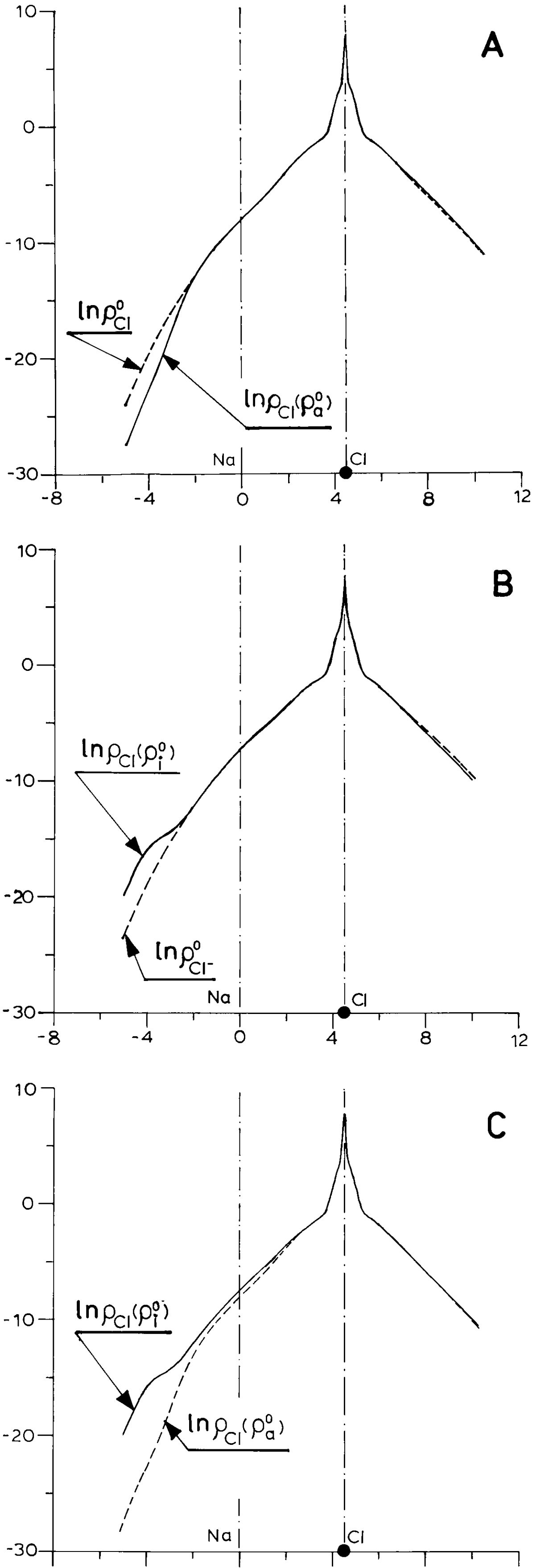
We therefore conclude from Figs. 1 and 2 that the ionic reference indeed generates the electron density which appears to be slightly less "displaced" from the molecular density. In the related Taylor expansions of the molecular density in powers of the density difference, $\Delta\rho = \rho - \rho_{\mathrm{s}}^0$, around ρ_s^0, $s = $ i,a, one should therefore obtain a slightly faster convergence for the ionic reference in comparison to the atomic one.

Therefore, one would also expect the ionic promolecule of NaCl to generate bonded atoms which are less displaced from the corresponding constituent ion densities, thus producing a faster converging Taylor expansion of the AIM density $\rho_\alpha\,(\rho_{\mathrm{i}}^0)$ in terms of powers of the atomic density displacement $\Delta\rho_\alpha\,(\rho_{\mathrm{i}}^0) = \rho_\alpha - \rho^0_{\alpha,\mathrm{i}}$, in comparison to the expansion of $\rho_\alpha\,(\rho_{\mathrm{a}}^0)$ in powers of $\Delta\rho_\alpha$ $(\rho_{\mathrm{a}}^0) = \rho_\alpha - \rho^0_{\alpha,\mathrm{a}}$. When using the ionic reference, however, one should always remember about the reverse direction of the associated CT, $\mathrm{CT_i}$, relative to the standard direction, $\mathrm{CT_a}$, conventionally linked to the atomic dissociation limit.

In chemistry, however, one always defines the CT relative to a common atomic reference. Therefore, one would also prefer a similar, universal reference in the Hirshfeld partitioning. It follows from Figs. 1 and 2 that settling for the atomic promolecule indeed should provide a very sound and natural universal reference in all the information-theoretic partitioning schemes.

4.3 Sodium atom/cation densities

Let us now examine in some detail the differences between the sodium bonded atoms resulting from the two alternative promolecule references of the Hirshfeld



◄ **Fig. 4A–C.** Same as in Fig. 3 for Cl. Here ρ^0_{Cl} and $\rho^0_{Cl^-}$ denote the electron densities of the isolated chlorine atom (SAL-a) and atomic anion (SAL-i), respectively

procedure, which are compared in the logarithmic plots of Fig. 3.

As shown in Fig. 3C, the two atomic densities, $\rho_{Na}(\rho^0_i)$ and $\rho_{Na}(\rho^0_a)$, differ mainly in the direction of the bonding partner, with the ionic promolecule giving rise to a faster decay of $\rho_{Na}(\rho^0_i)$ in comparison to $\rho_{Na}(\rho^0_a)$. This indicates that the atomic promolecule should lead to a slightly smaller AIM charge separation, in comparison to the ionic reference state. It should be emphasized, however, that the observed differences in density plots are only in the very low value region, so the changes in the magnitude of AIM charges will be very small indeed.

A reference to Fig. 3A shows a polarization of the $\rho_{NA}(\rho^0_a)$ density, relative to the isolated atom density ρ^0_{Na}. One indeed detects there a manifestation of the CT_a flow of the valence electrons from the nonbonding region of the sodium atom towards the chorine atom in NaCl. The reverse trend is observed in Fig. 3B, where the $\rho_{Na}(\rho^0_i)$ density is compared with the reference cation density, ρ_{Na^+}. This observation is again in agreement with the reverse direction of the CT for the ionic reference state, CT_i.

4.4 Chlorine atom/anion densities

The complementary set of logarithmic plots for the chlorine atom is presented in Fig. 4. As shown in Fig. 4C, the ionic promolecule generates slightly higher values of $\rho_{Cl}(\rho^0_i)$, relative to $\rho_{Cl}(\rho^0_a)$ in the bonding region, i.e., in the direction towards the sodium bonding partner. This again reflects a bit higher charge separation of the Hirshfeld atoms resulting from the ionic promolecule. We again point out, however, that these differences are noticeable only in the very low value region of the density. Thus, the two bonded chlorine AIM are for all practical reasons identical. The same general conclusion applies to the two sodium atom densities of Fig. 3C. In view of the observed weak dependence of the AIM electron densities on the selected promolecule reference a choice of the universal, atomic promolecule reference seems the most natural and unbiased one.

The reverse directions of the CTs relative to both promolecule states, CT_i and CT_a, are again reflected in the nonbonding side of Fig. 4A and B. In this region $\rho_{Cl}(\rho^0_a)$ is above the atomic reference ρ^0_{Cl} curve, while $\rho_{Cl}(\rho^0_i)$ is seen to be below the anionic reference $\rho^0_{Cl^-}$ plot.

5 Conclusion

A general conclusion following from the AIM densities of Figs. 3 and 4 is that the dependence of the Hirshfeld atoms on the promolecule reference is not a strong one. Both atomic and ionic promolecule atoms indeed exhibit single, almost identical cusps and to a very large extent they resemble the isolated atom/ion densities. For both sets of AIM appreciable differences are observed predominantly in the asymptotic, very low density regions of the valence shell. This is in agreement with the common knowledge that chemical atoms are only slightly perturbed relative to the isolated atoms/ions.

The dependence of the AIM densities on the selected promolecule reference should not come as a surprise. As explicitly reflected by the density difference diagrams, chemistry is the science of chemical bonds, i.e., "transitions" of constituent atoms, from their initial, nonbonded state in the atomic promolecule to the final, bonded state in a molecule. When extracting density changes due to molecular interaction one similarly compares the deviations of the density of the molecular complex relative to the procomplex density, of the isolated monomer densities shifted to the actual positions in the molecular complex, etc. Thus, the concept of a relevant reference is at the basis of most interpretations in chemistry. To avoid ambiguity one usually fixes the reference by agreeing on a common, universal choice. We believe we have demonstrated in this analysis that settling for the atomic promolecule density in the Hirshfeld procedure may indeed provide such a natural, standard reference in partitioning molecular densities into those of AIM, in full agreement with the accepted chemical definition of the direction of the CT in molecular systems. Finally, we emphasize that only in the atomic reference are the constituent atoms truly isolated and nonbonded, since in the ionic promolecule both atoms are linked by a single ionic bond.

It follows from the present numerical results that the densities of the Hirshfeld atoms in NaCl are only weakly dependent on the choice between the ionic and atomic promolecule densities. The ionic reference has been shown to lead to a slightly larger effective AIM charge separation; however, for all practical purposes, especially in the bonding region, the two sets of AIM densities are generally identical, thus demonstrating the remarkable insensitivity of the Hirshfeld partitioning scheme to a possible choice of the SAL. Obviously, the atomic reference of the accepted chemical definition of the CT is both the most natural and unbiased.

We have argued that the bonded atoms obtained from the ionic promolecule should be slightly less displaced with respect to the reference densities of isolated ions than are the bonded atoms resulting from the atomic promolecule – relative to the reference densities of isolated atoms. This is because the amount of $\mathrm{CT_i}$ is much less than that of $\mathrm{CT_a}$, since the molecular ground state for the equilibrium bond length is ionic in character. Only for this reason, and in accordance with the established chemical classification of the Na–Cl bond as ionic, would one perhaps also be interested in examining the ionic promolecule reference.

Finally, we address a more general question, whether one could envisage yet another molecularly promoted reference state of NaCl that would be even less displaced than the ionic promolecule. It should be recalled that the set of all possible dissociation states of a given molecular system is complete. Therefore, a search for the optimized promolecule density, ρ^0_{opt}, derived from a general combination of such SAL basis functions, which would resemble the most the molecular density ρ, would produce $\rho^0_{\mathrm{opt}} = \rho$.

In the NaCl case, however, one could also envisage the molecularly promoted reference density obtained from the SAL ensemble of the ionic and atomic promolecule densities. The ensemble average density, $\rho_{\mathrm{ens}}(\mathbf{r}; p)$, of such a statistical mixture is defined by the positive probabilities $p_{\mathrm{a}} = p$ and $p_{\mathrm{i}} = 1 - p$ of the two promolecule densities:

$$\rho_{\mathrm{ens}}(\mathbf{r};p) = p\rho^0_{\mathrm{a}}(\mathbf{r}) + (1-p)\rho^0_{\mathrm{i}}(\mathbf{r}) \ . \tag{18}$$

One would then search for the optimum $p = p^0_{\mathrm{a}}$ determining the "best" promolecule choice $\rho_{\mathrm{ens}} = \rho^0_{\mathrm{ens}}$ which minimizes deviations of ρ_{ens} from the known molecular density ρ:

$$\min_p \int [\rho_{\mathrm{ens}}(\mathbf{r};p) - \rho(\mathbf{r})]^2 \mathrm{d}\mathbf{r} = \int \left[\rho^0_{\mathrm{ens}}(\mathbf{r};\, p^0_a) - \rho(\mathbf{r})\right]^2 \mathrm{d}\mathbf{r} \ . \tag{19}$$

This least-squares procedure gives

$$p^0_{\mathrm{a}} = \int \left[\rho^0_{\mathrm{i}}(\mathbf{r}) - \rho^0_{\mathrm{a}}(\mathbf{r})\right]\left[\rho^0_{\mathrm{i}}(\mathbf{r}) - \rho(\mathbf{r})\right] \mathrm{d}\mathbf{r} \Big/ \int \left[\rho^0_{\mathrm{i}}(\mathbf{r}) - \rho^0_{\mathrm{a}}(\mathbf{r})\right]^2 \mathrm{d}\mathbf{r}. \tag{20}$$

Such an optimized ensemble of the ionic and atomic promolecule densities should produce an even less displaced reference state and thus even more precise AIM densities. In the future we intend to test the Hirshfeld AIM densities resulting from this optimized ensemble promolecule density. A similar procedure can be adopted in molecular systems, for example, molecular ions, exhibiting several possible candidates for the promolecule reference densities in both the ground and excited states.

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